云　南　植　物　研　究　2010，**32**（4）：378～380
**Acta Botanica Yunnanica**　DOI：10.3724/SP.J.1143.2010.10052

# 团花树中一个新的环烯醚萜苷*

刘玲丽[1,2]，朱　锋[1]，邸迎彤[1]，郝小江[1**]，何红平[1**]
（1 中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室，
云南 昆明　650204；2 中国科学院研究生院，北京　100049）

**摘要**：从茜草科团花属植物团花树（*Neolamarckia cadamba*）枝叶的甲醇提取物中分离得到两个环烯醚萜苷，其中一个为新的环烯醚萜苷，利用现代波谱学技术鉴定了其结构为 $\Delta^{13,14}$- plumieride，并命名为 plumieride B.

**关键词**：团花树；茜草科；环烯醚萜苷
**中图分类号**：Q 946　**文献标识码**：A　**文章编号**：0253-2700(2010)04-378-03

# Plumieride B, a New Iridoid from *Neolamarckia cadamba* (Rubiaceae)

LIU Ling-Li[1,2], ZHU Feng[1], DI Ying-Tong[1], HAO Xiao-Jiang[1**], HE Hong-Ping[1**]
(1 *State Key Laboratory of Phytochemistry and Plant Resources in West China*, *Kunming Institute of Botany*, *Chinese Academy of Sciences*, Kunming 650204, China;
2 *Graduate University of Chinese Academy of Sciences*, Beijing 100049, China)

**Abstract**: A new iridoid, named plumieride B, was isolated from the leaves of *Neolamarckia cadamba*, together with a known iridoid. The new structure was determined to be $\Delta^{13,14}$-plumieride by spectroscopic methods especially 2D-NMR analysis.

**Key words**: *Neolamarckia cadamba*; Iridoid; Rubiaceae

The species *Neolamarckia cadamba*, previously named *Anthocephalus chinensis*, is a member of the tribe Naucleeae in the family Rubiaceae and distributed widely in the south of China (Luo *et al.*, 1999; Zhong *et al.*, 1990). It has been used traditionally in "dai" ethnopharmacy by the local ethnic people in Yunnan Province of China to treat inflammation, fever and pruritus (Compiled group of Yunnan Traditional Chinese Medicine, 1977). Moreover, in India, it has been used in Ayurvedic medicine for blood diseases and dysentery (Takayama *et al.*, 2003). So far, the chemical constituents of *N. cadamba* have been extensively investigated and different types of compounds have been reported, including monoterpenoid indole alkaloids and iridoids (Zhou *et al.*, 2008; Brown *et al.*, 1976; Handa *et al.*, 1984, 1983). As part of a continuing effort to discover novel secondary metabolites from Yunnan local medicinal plants (Zhou *et al.*, 2008), a further chemical investigation on the leaves of *N. cadamba* was carried out, which led to obtain a new iridoid, plumieride B (**1**) and a known iridoid, plumieride (**2**) (Abe *et al.*, 1988). This paper reports the isolation and structure elucidation of plumieride B (**1**).

---

* Foundation item: The National Science Foundation of Yunnan Province (2009CD112)

** Author for correspondence; E-mail: haoxj@mail.kib.ac.cn, hehongping@mail.kib.ac.cn; Tel: +86-871-5223263. fax: +86-871-5223070

Received date: 2010-03-11, Accepted date: 2010-05-17

作者简介：刘玲丽（1984－）女，硕士研究生，研究方向为天然药物化学。E-mail：liulingli@mail.kib.ac.cn

## Results and Discussion

Plumieride B (**1**) was isolated as white solid. Its molecular formula was deduced to be $C_{21}H_{24}O_{11}$ on the basis of the positive HRESIMS at $m/z$ 475.1210 $[M+Na]^+$ (calcd 475.1216), which indicated ten degrees of unsaturation in **1**. Intensive absorption bands at 1764 and 1683 $cm^{-1}$ observed in IR spectrum suggested the presence of carbonyl groups. The $^{13}C$ NMR and DEPT spectra (Table 1) revealed 21 carbon signals due to three quaternary carbons, thirteen methines, two methylenes, two carbonyls and one methoxy group. The $^{13}C$ NMR data also exhibited characteristic signals of iridoids [$\delta_C$ 93.8 (d, C-1), 152.3 (d, C-2), 111.3 (s, C-4)]. Furthermore, it also displayed a signal of a quaternary carbon [$\delta_C$ 97.3 (s, C-8)], a typical signal of a rather rare group of iridoids containing a spiro-lactone ring. In the $^1H$ and $^{13}C$ NMR spectra, an anomeric proton signal at $\delta_H$ 4.64 (1H, d, $J = 7.9$ Hz, H-1′), and carbon signals [$\delta_C$ 99.8 (d, C-1′), 74.7 (d, C-2′), 77.8 (d, C-3′), 71.4 (d, C-4′), 78.4 (d, C-5′), 62.5 (t, C-6′)], indicated the presence of a glucose moiety in **1**. An extensive comparison of $^1H$ and $^{13}C$ NMR spectra of compound **1** with plumieride (**2**) (Abe *et al*., 1988) suggested that they shared similar planar structure except for a double bond between C-13 and C-14 in compound **1** instead of a hydroxyl at C-13 in plumieride (**2**).

The $^1H$-$^1H$ COSY revealed that **1** possessed two fragments, (**a**): (C-1 to C-9, C-9 to C-5, C-6 and C-7) and (**b**): (C-13 to C-14) (Fig. 1). In the HMBC spectrum of compound **1**, the correlations from H-14 to C-11 and C-12 indicated the linkage of unit **b**, the olefinic carbon and the carbonyl. Furthermore, the HMBC correlations of H-9/C-8, and H-9/C-10 suggested the fragment **a** linked to the fragment **b** via a quaternary carbon and two olefinic carbons. The similar $^1H$ and $^{13}C$ NMR data of compounds **1** and **2** at C-6, C-7, C-8, C-9, C-10 and C-12 indicated that compound **1** had a same spiro-lactone ring and the same relative configuration of C-8 as plumieride (**2**). In addition, the carboxylic methyl ester group was positioned at C-4 based on correlations of H-3/C-15 and $H_3$-16/C-15 in the HMBC spectrum. The HMBC correlation of H-1/C-1′ established the linkage of glucose substituent to C-1. Detailed 2D NMR analysis further established the planar structure of **1**. The relative configuration of **1** was determined by ROESY analysis and coupling constant. The orientations of H-1, H-5 and H-9 were assigned to be the same as compound **2** because of their approximate chemical shifts and coupling constants. The coupling constant of H-1′ ($J = 7.9$) deduced the glucose to be a $\beta$-oriented, and the glucose was assigned to be D-glucose, the same as other iridois of this type (Abe *et al*., 1984). Thus, compound **1** was determined as shown in Fig. 2.

## Experimental

**General Experimental Procedures** 1D and 2D NMR spectra were recorded on Bruker AM-400 and DRX-500 spectrometers with TMS as internal standard, respectively. Optical rotations were measured on a JASCO DIP-370

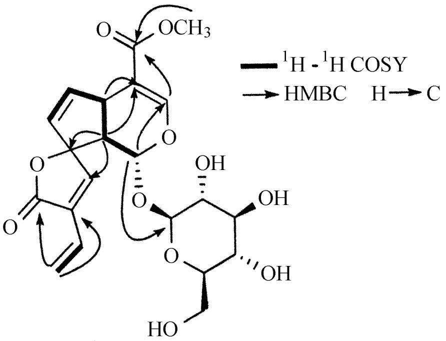
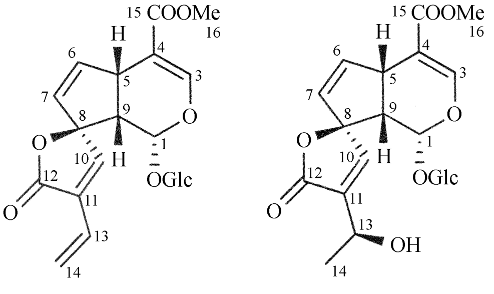


Fig. 1 Key HMBC and COSY correlations of compound **1**



**compound 1**　**compound 2**

Fig. 2 Structures of compounds **1** and **2**

**表1 化合物 Plumieride B (1) 与 Plumieride (2) 的氢谱和碳谱数据**

Table 1 The 1D NMR data of Plumieride B (**1**) and Plumieride (**2**) in $CD_3OD$

| No. | **1** | | **2** | |
|---|---|---|---|---|
| | $\delta_H$ | $\delta_C$ | $\delta_H$ | $\delta_C$ |
| 1 | 5.29 (d，4.4) | 93.8 d | 5.26 (d，4.7) | 94.1 d |
| 3 | 7.47 (s) | 152.3 d | 7.48 (s) | 152.4 d |
| 4 | | 111.3 s | | 111.0 s |
| 5 | 3.88 (m) | 39.9 d | 3.91 (m) | 40.3 d |
| 6 | 6.46 (dd，5.5，2.9) | 141.1 d | 6.45 (dd，5.6，2.5) | 141.4 d |
| 7 | 5.50 (dd，5.5，1.6) | 129.8 d | 5.51 (dd，5.6，2.0) | 130.0 d |
| 8 | | 97.3 s | | 97.9 s |
| 9 | 2.95 (dd，6.2，3.6) | 50.9 d | 2.93 (dd，7.7，4.8) | 50.5 d |
| 10 | 7.36 (s) | 150.8 d | 7.34 (s) | 150.2 d |
| 11 | | 130.1 s | | 138.6 s |
| 12 | | 172.3 s | | 172.8 s |
| 13 | 6.46 (m) | 126.7 d | 6.45 (m) | 63.5 d |
| 14 | 5.49 (dd，14.4，1.6) | 121.8 t | 1.39 (d，6.5) | 22.4 q |
| 14 | 6.25 (dd，14.4，1.6) | | | |
| 15 | | 168.4 s | | 168.4 s |
| 16 | 3.74 (s) | 51.9 q | 3.74 (s) | 51.9 q |
| 1′ | 4.64 (d，7.9) | 99.8 d | 4.66 (d，7.9) | 100.0 d |
| 2′ | 3.12 (m) | 74.7 d | 3.17 (m) | 74.6 d |
| 3′ | 3.31 (m) | 77.8 d | 3.33 (m) | 77.8 d |
| 4′ | 3.23 (m) | 71.4 d | 3.18 (m) | 71.3 d |
| 5′ | 3.24 (m) | 78.4 d | 3.28 (m) | 78.4 d |
| 6′ | 3.62 (dd，10.5，5.5)<br>3.84 (m) | 62.5 t | 3.67 (dd，11.0，5.5)<br>3.86 (m) | 62.5 t |

[a] $^1H$ and $^{13}C$ NMR spectra were obtained at 400 and 100 MHz，respectively

[b] Coupling constants were presented in Hertz，unless otherwise indicated，all proton signals integrate to 1H

digital polarimeter. A Tenor 27 spectrophotometer was used for scanning IR spectroscopy. ESIMS was recorded on a finnigan MAT 90 instrument，HRESIMS spectrum on VG Auto Spec-3000 spectrometer. Column chromatography was performed on silica gel (200－300 mesh; Qingdao Marine Chemical Inc.，Qingdao，People′s Republic of China)，Sephadex LH-20 (40－70 μm，Amersham Pharmacia Biotech AB，Uppsala，Sweden)，and Lichroprep RP-18 gel (40－63 μm，Merck Darmstadt，Germany).

**Plant material** The air-dried leaves of *N. cadamba* (25 kg) were collected in Xishuangbanna，Yunnan Province of China in July，2008. The plant was identified by Prof. Xun Gong，Chinese Academy of Science. A specimen of this plant (No. 0766725) was deposited in the Kunming Institute of Botany，Kunming，China.

**Extraction and isolation** The dried and powdered leaves of *N. cadamba* (25 kg) were refluxed three times with 90% EtOH. The solvent was evaporated in vacuo to obtain a crude extract. After suspending in water，the crude extract was extracted successively with petroleum ether，EtOAc，and n-BuOH. The n-BuOH extract (180 g) was subjected on RP (reverse phase) -18 eluting with $H_2O$-MeOH (from 10 ∶ 1 to 0 ∶ 10) to afford five fractions (I-V). Fraction IV (20 g) was further chromatographed on silica gel using $CHCl_3$-MeOH [$CHCl_3$-MeOH (10 ∶ 1)，(5 ∶ 1) and (3 ∶ 2)] to give three fractions A，B，and C. Fraction B was purified by Sephadex LH-20 (eluted with MeOH) and a series of silica gel column chromatography to afford compounds **1** (12 mg) and **2** (53 mg).

Plumieride B (**1**): $C_{21}H_{24}O_{11}$，white solid; $[\alpha]_D^{20}=-93.5$ ($c=0.12$，MeOH); Positive ESIMS *m/z* 475 $[M+Na]^+$; HRESIMS *m/z* 475.1210 $[M+Na]^+$ (calcd 475.1216). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3423，1764，1683，1639，1444，1294，1178，1081，1035，997，871; $^1H$ and $^{13}C$ NMR data，see Table 1.

Plumieride (**2**): $C_{21}H_{26}O_{12}$，white solid，$[\alpha]_D^{24}=-38.1$ [$c=0.32$，$CHCl_3$+MeOH (1 ∶ 1)]; $^1H$ and $^{13}C$ NMR data，see Table 1.

## References:

Abe F，Mori TJ，Yamauchi T，1984. Iridoids of Apocynaceae III. Minor iridoids from *Allamanda neriifolia* [J]. *Chemical & Pharmaceutical Bulletin*，**32** (8): 2947—2956

Abe F，Chen RF，Yamauchi T，1988. Minor iridoids from the roots of *Plumeria acutifolia* [J]. *Chemical & Pharmaceutical Bulletin*，**36** (8): 2784—2789

Brown RT，Chappel CL，1976. Anthocephalus alkaloids: Cadamine and isocadamine [J]. *Tetrahedron Letters*，**17** (19): 1629—1630

Compiled Group of Yunnan Traditional Chinese Medicine，1977. Yunnan Tradutional Chinese Medicinal Plant [M]. Kunming: Yunnan People′s Press，36

Luo XR，Ko WC，Chen WC *et al.*，1999. Flora of China [M]. Beijing: Science Press，**71** (1): 261

Handa SS，Gupia S，Vasisht K *et al.*，1984. Quinoline alkaloids from *Anthocephalus chinensis* [J]. *Planta Medica*，**50** (4): 358

Handa SS，Borris RP，Cordell GA *et al.*，1983. NMR spectral analysis of cadambine from *Anthocephalus chinensis* [J]. *Journal of Natural Products*，**46** (3): 325—330

Zhou H，He HP，Kong NC *et al.*，2008. Indole alkaloids from the leaves of *Anthocephalus chinensis* [J]. *Helvetica Chimica Acta*，**91**: 2148—2152

Takayama H，Tsutsumi SI，Kitajima M *et al.*，2003. Gluco-indole alkaloids from *Nauclea cadamba* in Thailand and transformation of 3α-Dihydrocadambine into the indolopyridine alkaloid 16-Carbomethoxynaufoline [J]. *Chemical & Pharmaceutical Bulletin*，**51** (2): 232—233

Zhong JY，Wang WR，Zhang ZX *et al.*，1990. Chemial consitituents from the bark of *Anthocephalus chinensis* [J]. *Acta Botanica Yunnanica*，**12** (4): 453—456